Supplementary Information

In the following supplementary sections, we present details of the experimental methods used, additional data from electrical measurements (figures 1s-4s), FTIR raw data (figure 5s), XRD data on grain sizes (figure 6s) and phase segregation in GeTe (figure 7s) and a variable range hopping fit to the low temperature regime of the resistivity for Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4} (figure 8s).

A discussion of the limit of the Drude contribution for small scattering times reveals that in this regime, only upper limits for the scattering time and lower limits for the plasma frequency can be determined. Moreover, the doping and transport mechanisms in GeTe are addressed. In addition we discuss the static dielectric constant of Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4} and a possible scenario for the structural rearrangements upon annealing. In this context we show evidence suggesting that the presence of empty lattice sites is crucial for the formation of the insulating state in Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4}.

Finally, we list the annealing temperatures of samples investigated in figure 2.

Methods

(1) Sample preparation and annealing: Thin film samples with thicknesses between 80 nm and 1000 nm were sputter deposited (DC magnetron) on cleaned glass substrates for van-der-Pauw and Hall measurements. Aluminum coated glass substrates were used for optical (FTIR, ellipsometry) and XRD experiments. (Further details are given in\textsuperscript{35}.)

The samples were annealed in argon atmosphere (flow rate of 200 sccm) in a regular tube furnace with a 3 cm diameter quartz tube. The annealing procedure started at room temperature, where a constant heating rate of 5 K/min was applied and the holding time at the anneal temperature was 30 min. After this period, the sample was cooled to a temperature of 80 °C, and then extracted from the furnace.

(2) The electrical measurements (Hall and resistivity) were performed in van-der-Pauw geometry\textsuperscript{20} on samples directly deposited on glass substrates. Contacts were either fabricated via thermal evaporation of gold (50 nm) or sputter deposition of chromium (~100 nm) through shadow masks. The measurements shown in figures 1, 2 and 4s were performed using chromium contacts, the measurements shown in figures 3, 4, 1s, 2s, 3s and 8s were performed using gold contacts.

The low-temperature measurements were carried out in a home-built glass cryostat-based setup. Hall and van-der-Pauw measurements utilize custom designed setups with signal
amplification close to the sample to ensure high sensitivity and a large enough dynamic range to follow the large change in resistivity upon crystallization and step-annealing.

**Determination of the electrical transport parameters**

Combining Hall and resistivity measurements as well as optical spectroscopy results, it is possible to determine the charge carrier parameters within the framework of a degenerately doped semiconductor where the Fermi level is located within the valence band. When calculating the Fermi wave vector or related quantities, the multiplicity $M$ of the corresponding valence band maximum must be taken into account. In the literature, the relevant valence band maximum for IV-VI compounds (GeTe$^{49,50}$, PbTe$^{49,51}$) is given at the L-point, where the band shows a four-fold degeneracy. Consequently, we assume the same four-fold multiplicity ($M=4$) in all calculations for GeTe as well as step-annealed Ge$_1$Sb$_2$Te$_4$.

1. Fermi wave vector
   $$k_F = \left[ 3\pi^2 \frac{n_{Hall}}{M} \right]^{\frac{1}{3}}$$

2. Effective mass
   $$\frac{m^*}{m_e} = \frac{n_{Hall}}{n \cdot \frac{m_e}{m^*}}_{FTIR}$$

3. Fermi energy
   $$E_F = \frac{\hbar^2 k_F^2}{2m^*}$$

4. Fermi velocity
   $$v_F = \frac{\hbar k_F}{m^*}$$

5. Mobility
   $$\mu = \frac{\sigma_{vdP}}{e \cdot n_{Hall}}$$

6. Mean free path
   $$\lambda = \frac{\hbar}{e^2 \sigma_{vdP} \left[ \frac{3\pi^2}{n_{Hall}^2 M} \right]^{\frac{1}{3}}}$$

7. Conductivity ratio
   $$r_e = \frac{\sigma_{measured}}{\sigma_{min}} = \frac{\sigma_{measured}}{\rho_{max}}$$

**Drude contribution in the regime of small scattering times**

The FTIR data were analyzed using a semiconductor model (Tauc-Lorenz oscillator) with a free electron Drude contribution (see $^{35}$ for details).

In the limit of very small scattering times the Drude contribution becomes
\( \chi(\omega) = \frac{\alpha^2}{\omega^2 \cdot e^{\omega \tau}} \rightarrow \omega \ll \omega_p \quad i \frac{\omega^2 \tau}{\epsilon_0} \cdot \frac{i}{\omega} \)

with \( \omega_p \) the plasma frequency of the free electron gas. Hence, in the limit (\( \tau \ll \omega_p \)), it is only possible to determine the product of \( \tau \) and \( \omega_p \) (the conductivity \( \sigma \)). For this reason, only an upper limit for the scattering time can be determined. The Drude model fails to reproduce the optical spectra if the scattering time is chosen to be too large, but the fitting procedure becomes unstable in the case of very small scattering times.

**Remarks on the doping mechanism in GeTe**

In phase change materials the Fermi energy typically resides in the valence band close to the valence band maximum. This is due to the formation of vacancies on the cation sublattice as proven by DFT calculation of Edwards et al.$^{52}$ for GeTe. These computations reveal that it is energetically favorable to form Ge vacancies in stoichiometric GeTe. It is interesting to note that the carrier concentration observed for GeTe is in line with the vacancy concentration, confirming the assumption that these vacancies create the carriers observed in GeTe.

**Discussion of the electrical transport mechanism in GeTe**

For GeTe, the conductivities derived from optical and electrical measurements displayed in figure 2s agree within a factor of 1.8, and the scattering time is determined to 2.4 fs. From the plasma-frequency, a ratio of carrier concentration vs. effective mass of \( n \times m_e / m^* \sim 1.5 \) - \( 2.0 \times 10^{21} \) cm\(^{-3} \) is obtained. This ratio together with the Hall carrier concentration yields an effective mass of about 0.3 m\(_e\), in good agreement with\(^{22,53,54}\). Thus, GeTe is a degenerate semiconductor. Due to the fourfold band degeneracy of the valence band maximum at the L-point, the Fermi level lies about 0.35 eV below the valence band edge. The linear increase of the Seebeck coefficient with temperature (data not shown) in conjunction with the positive Hall coefficient confirms GeTe to be a degenerate p-type semiconductor.

**Evaluation of the maximum metallic resistivity/minimum metallic conductivity for GeTe**

According to table 1s, the Fermi wave vector is about \( 1.59 \times 10^7 \) cm\(^{-1} \). Consequently, a maximum metallic resistivity of \( \rho_{\text{max}} = 3\pi^2 h/4e^2 k_F = 1.91 \) m\( \Omega \) cm (523 S/cm) is obtained for GeTe. As expected for a degenerate semiconductor the observed (actual) conductivity is always much larger than minimum metallic conductivity. This can be seen from the high values of \( r_\sigma \) in table 1s and figure 2s.
Remarks on the static dielectric constant in Ge$_2$Sb$_2$Te$_4$

The optical dielectric constant $\varepsilon_\infty$ obtained from FTIR measurements is larger than 30. However, to our knowledge, no experimental values for $\varepsilon_{st}$ of Ge$_2$Sb$_2$Te$_4$ are available at present. Since phase change materials have soft phonon modes $\varepsilon_{st}$ is significantly larger than $\varepsilon_\infty$, as can be seen from the Lyddane-Sachs-Teller relationship\(^1\). Our DFT calculations estimate $\varepsilon_{st}$ to be at least 98\(^3\).

Estimation of the grain sizes in GeTe and Ge$_2$Sb$_2$Te$_4$

The full width at half maximum (FWHM) of the (200) reflection from the cubic unit cell of GeTe and Ge$_2$Sb$_2$Te$_4$ samples processed at different annealing temperatures were measured at room temperature and are shown in figure 6s. The grain size was estimated using the Scherrer formula. The FWHM indicates grain sizes of the order of 20 – 40 nm for GeTe, and of the order of 10 to 20 nm for Ge$_2$Sb$_2$Te$_4$, in good agreement with the value of approximately 20 nm determined by \(^{40}\). However, the separation of strain and size effects is not possible in an unambiguous way, and the values therefore represent the lower limit, since strain broadening and size broadening are additive. Comparing the obtained grain size values with the electronic mean free paths in GeTe and Ge$_2$Sb$_2$Te$_4$, it is evident that grain boundary scattering cannot be the dominant scattering channel.

Structural rearrangements and the role of empty lattice sites in Ge$_2$Sb$_2$Te$_4$

It was recently shown that in Ge$_2$Sb$_2$Te$_4$ strong positional disorder on the cation lattice is also present\(^{34}\), in addition to the atomic disorder and large number of empty lattice sites. This raises the question: Which type of disorder is more pronounced in producing the strong localization effects: empty lattice sites on the cation lattice, or positional disorder. We therefore investigated Ge$_3$Sn$_1$Te$_4$, a ternary phase change material without empty lattices, but cation disorder as well as positional disorder. As can be seen in figure 4s, both GeTe and Ge$_3$Sn$_1$Te$_4$ behave very similar and the conductivity barely changes after the initial crystallization. Therefore, we conclude that the empty lattice sites play a crucial role in reducing the electrical conductivity in these phase change materials.

One may speculate on the microscopic mechanism responsible for the gradual disappearance of disorder with annealing temperature: Upon initial crystallization, the tellurium atoms form an fcc sublattice \(^{40,43}\). This fast process will produce a random arrangement of germanium, antimony and empty lattice sites on the cation sublattice of the rocksalt-structure. Upon annealing the empty lattice sites will enable Ge/Sb diffusion preparing the transition to the stable hexagonal phase which is accompanied by ordering of the empty lattice sites into [111] (previously cubic)
planes, and some additional ordering of Ge and Sb on the remaining cation sites. Thus, it is clear that the empty lattice sites are playing an important role in the development of the electronic transition from localized to delocalized charge carriers.

**Annealing Temperatures in Figure 2**

The data points depicted in figure 2 have been obtained after annealing samples of the corresponding materials to the following temperatures:

<table>
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<th>T / °C</th>
<th>150</th>
<th>175</th>
<th>200</th>
<th>225</th>
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<th>300</th>
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<td>x</td>
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<td>x</td>
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Figure 1s: Resistivity of Ge₁Sb₂Te₄ films between 5 and 300 K

The resistivity for 4 samples annealed in the range from 250 °C to 325 °C is displayed. For an annealing temperature of 250 °C non-metallic, i.e. a negative TCR is observed. The resistivity of the samples annealed to high temperatures (300 °C and 325 °C) remains metallic in the whole range. It is noteworthy, that the critical boundary resistivity between metallic and insulating behavior is valid in the whole temperature range. The sample annealed to 275 °C falls right into this transition regime.
Figure 1s: Resistivity of Ge1Sb2Te4 films between 5 and 300 K. The resistivity for 4 samples annealed in the range from 250 °C to 325 °C is displayed. For an annealing temperature of 250 °C non-metallic, i.e. a negative TCR is observed. The resistivity of the samples annealed to high temperatures (300 °C and 325 °C) remains metallic in the whole range. It is noteworthy, that the critical boundary resistivity between metallic and insulating behavior is valid in the whole temperature range. The sample annealed to 275 °C falls right into this transition regime.

Figure 2s: Annealing temperature dependence of the electrical transport parameters of GeTe films measured at room temperature.

Shown from top to bottom is the electrical conductivity $\sigma$, the carrier density, the mobility $\mu$, and the conductivity ratio $r_\sigma = \sigma_{\text{measured}} / \sigma_{\text{min}}$. Values derived from electrical measurements (Hall and van-der-Pauw) are shown as red squares; results from optical measurements (FTIR) are shown as blue diamonds.

Besides the small effect due to Ge segregation occurring between 225 and 250°C (figure 6s), almost no annealing temperature dependence of the transport parameters can be observed. As expected for degenerate semiconductors, the conductivity ratio $r_\sigma$ is significantly larger than 1.
Figure 3s: Resistivity of GeTe films below 300 K

The data for two films annealed to 225°C and 250°C is depicted. The small change upon annealing already visible in figure 1s can be observed again. At both annealing temperatures the temperature dependence is clearly metallic (no freeze-out and TCR >0). As the room-temperature resistivity is constant from 250 to 325°C (see figure 1s) there is no reason to assume further changes of ρ(T) in this region.

Figure 4s: Temperature dependent sheet resistance of Ge₃Sn₁Te₄ upon annealing

Starting in the amorphous phase the sheet resistance decreases and drops rapidly due to the crystallization of the film at 160°C. The temperature dependence is very similar to the one observed for GeTe (see figure 1), with a reduced crystallization temperature due to the partial
substitution of germanium by tin. Note the absence of a pronounced change of resistance with higher temperature for the crystalline phase.

Figure 3s: Resistivity of GeTe films below 300 K

The data for two films annealed to 225°C and 250°C is depicted. The small change upon annealing already visible in figure 1s can be observed again. At both annealing temperatures the temperature dependence is clearly metallic (no freeze-out and TCR > 0). As the room-temperature resistivity is constant from 250 to 325°C (see figure 1s) there is no reason to assume further changes of \( \rho(T) \) in this region.

Figure 4s: Temperature dependent sheet resistance of Ge\textsubscript{3}Sn\textsubscript{1}Te\textsubscript{4} upon annealing

Starting in the amorphous phase the sheet resistance decreases and drops rapidly due to the crystallization of the film at 160°C. The temperature dependence is very similar to the one observed for GeTe (see figure 1), with a reduced crystallization temperature due to the partial substitution of germanium by tin. Note the absence of a pronounced change of resistance with higher temperature for the crystalline phase.

Figure 5s: Infrared reflectance spectra of GeTe and Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4} thin films on aluminum

The measurements were performed at room temperature after different annealing treatments. The reflectance spectra of the GeTe film (0.66 \( \mu \)m) display the Drude feature at lower energies and the onset of the interband transition at higher energies. Between these two features periodic Fabry-Perot interferences typical for transparent thin films can be observed. Besides the small shift from 225°C to 250°C caused by Ge segregation (see figure 6s) annealing has no effect on spectra of GeTe. The Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4} film (1.05 \( \mu \)m), however, shows a gradual enhancement of the free carrier absorption visible in the continuously decreasing amplitude of the signal upon annealing. Thus, the optical conductivity shows the same trend as the DC conductivity (see figure 4).
Figure 6s: FWHM of GeTe and Ge$_1$Sb$_2$Te$_4$ films upon annealing

Full width at half maximum (FWHM) of the (200) diffraction peak of the cubic unit cell of GeTe and Ge$_1$Sb$_2$Te$_4$ as a function of annealing temperature. The spectra were measured with Cu K$_\alpha$ radiation in grazing incidence geometry ($\omega=1^\circ$). For both materials the FWHM decreases continuously with higher annealing temperatures. GeTe crystallizes into the rhombohedral phase after annealing to 225°C. The decrease of the FWHM is accompanied by Ge segregation at 250°C (figure 6s). Ge$_1$Sb$_2$Te$_4$ crystallizes at 150°C into the metastable cubic phase. Subsequent annealing results in the transition to the hexagonal phase at 250°C.
Figure 6s: FWHM of GeTe and Ge₁Sb₂Te₄ films upon annealing.

Full width at half maximum (FWHM) of the (200) diffraction peak of the cubic unit cell of GeTe and Ge₁Sb₂Te₄ as a function of annealing temperature. The spectra were measured with Cu Kα radiation in grazing incidence geometry (ω = 1°). For both materials the FWHM decreases continuously with higher annealing temperatures. GeTe crystallizes into the rhombohedral phase after annealing to 225 °C. The decrease of the FWHM is accompanied by Ge segregation at 250 °C (figure 6s). Ge₁Sb₂Te₄ crystallizes at 150 °C into the metastable cubic phase. Subsequent annealing results in the transition to the hexagonal phase at 250 °C.

Figure 7s: Germanium segregation in GeTe films.

At annealing temperatures of 250 °C and above Germanium peaks appear at 27.3° in the X-ray diffraction patterns accompanied by an increase of the GeTe lattice parameter.

Figure 8s: Fit of the low temperature resistivity for Ge₁Sb₂Te₄ annealed to 150 °C.

The low temperature dependence of the resistivity for Ge₁Sb₂Te₄ annealed at 150 °C is in excellent agreement with Mott’s model for variable range hopping\(^2\) \((\log \rho \propto T^{-0.25})\). The slowly growing deviation starting at about 50 K indicates a change of the transport mechanism towards higher temperatures.
Table 1: Summary of the transport parameters derived from optical and electrical measurements for GeTe.

The electrical conductivity $\sigma$, the carrier density $n$, the mobility $\mu$, the scattering time $\tau$, the effective mass $m^*$, the Fermi wave vector $k_F$, the Fermi energy $E_F$, the mean free path $\lambda$ and the conductivity ratio $r$ are listed for GeTe. Hall and van-der-Pauw derived parameters are shown in red, FTIR based parameters are shown in blue. The trends in these parameters are also displayed and discussed in figure 1s. All numbers have been calculated within the framework of a degenerately doped semiconductor assuming a four-fold multiplicity of the valence band maximum.

<table>
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<tr>
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Table 1: Summary of the transport parameters derived from optical and electrical measurements for GeTe. The electrical conductivity $\sigma$, the carrier density $n$, the mobility $\mu$, the scattering time $\tau$, the effective mass $m^*$, the Fermi wave vector $k_F$, the Fermi energy $E_F$, the mean free path $\lambda$ and the conductivity ratio $r_\sigma$ are listed for GeTe. Hall and van-der-Pauw derived parameters are shown in red, FTIR based parameters are shown in blue. The trends in these parameters are also displayed and discussed in figure 1s. All numbers have been calculated within the framework of a degenerately doped semiconductor assuming a four-fold multiplicity of the valence band maximum.

References


38Lencer, D. private communication.


